Short communication

Immersed effects of Ta and Zr compounds on activity of oxygen reduction reaction in sulfuric acid

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ABSTRACT

The immersed effects of Ta and Zr compounds (Ta–CNO and Zr–CNO) on the activity of oxygen reduction reaction (ORR) have been investigated in the sulfuric acid. The concentration of Zr on Zr–CNO was higher than that of Pt on Pt black. The concentration of Ta on Ta–CNO was almost the same as that of Pt on Pt black in sulfuric acid. The catalytic activity of Zr–CNO for the ORR decreased with time. In contrast, the catalytic activity of Ta–CNO for the ORR was maintained up to 1050 h in the sulfuric acid.

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1. Introduction

In order to establish a sustainable society, green hydrogen, which is produced using renewable energies, would be inevitable [1]. A high number of fuel cells and water electrolyzers must work in this system, and non-precious metal catalysts would be necessary because of the limited natural resources of precious metals.

To overcome these problems, we have focused on the group 4 and 5 transition metal compounds as non-precious metal electrocatalysts, and reported high catalytic activities of partially oxidized tantalum carbonitride (Ta–CNO) and zirconium carbonitride (Zr–CNO) for the oxygen reduction reaction (ORR). Not only the catalytic activity but also the stability of a material is very important factors to use them as the electrocatalyst of devices. The degradation of the electrochemical activity might be affected by chemical and electrochemical reactions. For the Pt electrocatalyst, there have been many studies reporting the stability of the Pt electrocatalyst under potential cyclings as an electrochemical evaluation simulating real applications [2,3]. The studies of the group 4 and 5 elements are very limited. We have reported the chemical stabilities such as the solubility of TaO_xN_y and ZrO_xN_y, etc. [4–6]. However, the dissolution amounts of Ta–CNO and Zr–CNO and the immersed effects of ORR activity of them have never researched in sulfuric acid, and it should be investigated for the development of non-precious metal material.

In this study, we have investigated the immersed effects of Ta–CNO and Zr–CNO in sulfuric acid on the activity of the oxygen reduction reaction (ORR) in order to evaluate the chemical stabilities of Ta–CNO and Zr–CNO.

2. Experimental

2.1. Preparation and dissolution measurement of Ta–CNO and Zr–CNO

$TaC_{0.58}N_{0.42}$ and Zr_2CN (A. L. M. T. Corp., Ltd.) were used as the raw materials. The Zr–CNO and Ta–CNO powders were obtained by the partial oxidation of the $TaC_{0.58}N_{0.42}$ or Zr_2CN under a 4% H_2/ 100–1000 ppm O_2/N_2 atmosphere at 1173 K for 5–40 h and at 1273 K for 10–60 h in a rotary electric furnace (Suntech Corp., Japan). The Ta–CNO and Zr–CNO were immersed in 1.0 M H_2SO_4 at room temperature up to 1050 h (=45 days). The concentration of Ta–CNO or Zr–CNO in sulfuric acid was determined by ICP-AES (SPS3000, SII, Japan) or ICP-MS (Agilent 7700x, Agilent

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Technologies, U.S.A). Particle sizes before and after the immersion were observed by FE-SEM (JSM-7001F, JEOL, Japan). Both the Ta–CNO and Zr–CNO before and after the immersion were identified by X-ray diffraction (XRD; XRD-6000, Shimadzu, Japan), and then evaluated the degree of oxidation (*DOO*) [4–6], which is the ratio of the main peak area of the oxides by XRD to the summation of the main peak area of the oxide and the carbonitride.

2.2. Electrochemical measurement of Ta–CNO and Zr–CNO before and after immersion in sulfuric acid

All the electrochemical experiments were carried out in a three-electrode cell with a reversible hydrogen electrode (RHE) as the reference electrode and the carbon plate as the counter electrode in 0.1 M H_2SO_4 at 303 K. The Ta–CNO and Zr–CNO with and without Ketjen Black EC300J (KB), which were supported by Nafion® on a glassy carbon ($\phi = 5.2$ mm, Tokai Carbon Corp., Ltd) or Ti rod ($\phi = 5.0$ mm, Nilaco Corp., Japan), were used as the working electrodes. All the electrochemical measurements were performed using a potentiostat (Model PS-04, Toho Technical Research, Japan) and function generator (FG-02, Toho Technical Research, Japan).

3. Result and discussion

3.1. Dissolution amounts of Ta–CNO and Zr–CNO

Fig. 1 shows the concentration of Zr (C_{Zr}) on the Zr–CNO in sulfuric acid as a function of the *DOO*. The concentrations of Zr on Zr_2CN as the raw material and Zr of the commercially available ZrO_2 are also in this figure. The Zr on Zr_2CN (*DOO* of 0.00) showed the highest C_{Zr}, while the commercial ZrO_2 showed the lowest C_{Zr} in these samples. The C_{Zr} of Zr–CNO decreased with the increase in the *DOO*. Although the Zr–CNO with the *DOO* of 0.95 had the lowest C_{Zr} of 2.95×10^{-4} mol dm^{-3}, it was still 100 times higher than the C_{Pt} ($= 3 \times 10^{-6}$ mol dm^{-3}) [7]. As a result, the carbonitride might be easy to dissolve in sulfuric acid. Since the oxide that formed on the surface of the Zr compounds increased with the *DOO*, the oxide layer might suppress the dissolution.

Fig. 2 shows the concentration of Ta (C_{Ta}) on the Ta–CNO in sulfuric acid as a function of the *DOO*. The concentration of Pt black [7], Ta on $TaC_{0.58}N_{0.42}$ as the raw material, and Ta on commercially
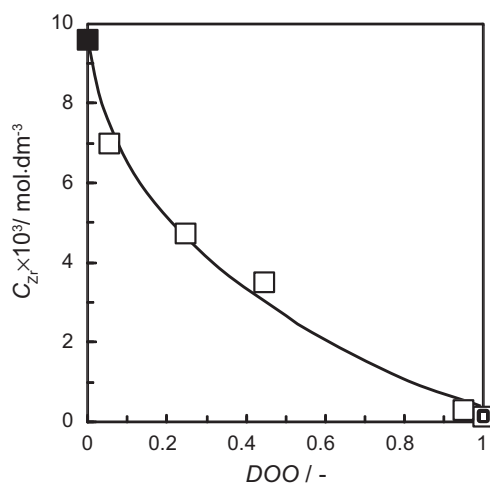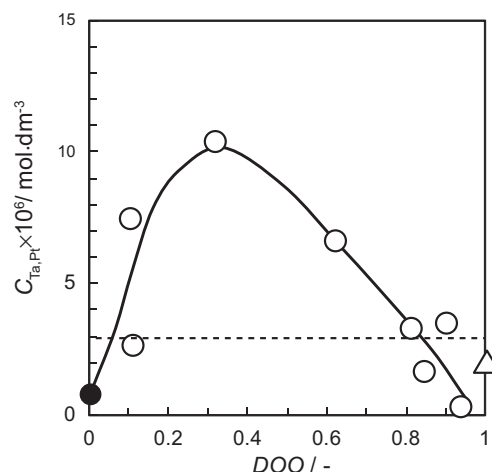
Fig. 2. Concentration of Ta on Ta–CNO before and after immersion in 1.0 M H_2SO_4 (●: Ta on $TaC_{0.58}N_{0.42}$, ○: Ta on Ta–CNO, Δ: Ta on Ta_2O_5 (commercial), – – – – –: Pt on Pt black).

available Ta_2O_5 are also in this figure. The C_{Ta} of the raw material with a high *DOO* (>0.80) was lower than the C_{Pt} of Pt black [7]. The C_{Ta} increased with an increase in the *DOO* up to 0.32. The highest C_{Ta} was at the *DOO* of 0.32, and was 10.4×10^{-5} mol dm^{-3}. Though some of the C_{Ta}s were higher than the C_{Pt} of Pt black, the C_{Ta}s were almost the same as the C_{Pt}. It is unclear why the concentration of Ta on Ta–CNO had a peak at the *DOO* of 0.32. However, the partial oxidation of tantalum carbonitride was found that the oxide layer is formed on the surface, and then would gradually be oxidized toward the inside of particle by our previous reports [6]. It was also reported that the carbon and nitrogen of tantalum carbonitride reacted to CO_2 and N_2 during the process of partial oxidation [8], and then the particle became the porous structure [6]. In addition, the oxide which was formed around the surface during the partial oxidation was suggested to the amorphous Ta_2O_5. Therefore, the phenomena that the concentration of Ta on Ta–CNO had a peak at *DOO* of 0.32 in Fig. 2 might be related to the amorphous oxide which was formed during the partial oxidation of tantalum carbonitride. As a result, the concentration of Ta on Ta–CNO with a high *DOO* was lower than that of Pt in sulfuric acid. It was also found that the Ta–CNO had a higher chemical stability than the Zr–CNO in sulfuric acid. The *DOO* of Ta–CNO hardly changed after the immersion because of their high chemical stability. In addition, the 1 μm particle sizes of the Ta–CNO before and after the immersion were almost the same.

3.2. Oxygen reduction reaction of Ta–CNO and Zr–CNO before and after immersion in sulfuric acid

Fig. 3 shows the Tafel plots for the ORR on Zr–CNO with several *DOO*s before and after the immersion in 1.0 M H_2SO_4. The i_{ORR} ($= i_{O_2} - i_{N_2}$) is based on the geometric surface area [4–6]. The slopes in the higher $|i_{ORR}|$ region (10 μA cm^{-2} < $|i_{ORR}|$) were -150 mV dec^{-1} for all the Zr–CNOs before and after their immersion. In the smaller $|i_{ORR}|$ region ($|i_{ORR}| < 3$ μA cm^{-2}), the Tafel slopes of Zr–CNO with the *DOO* of 0.99 changed after the immersion and was almost the same as that with the *DOO* of 0.25 before the immersion. It is unclear why the Tafel slopes changed in the smaller $|i_{ORR}|$ region. The surface might change on the Zr–CNO and affect the rate determining steps for the ORR of Zr–CNO.

Fig. 4 shows the Tafel plots for the ORR of Ta–CNO with the *DOO* of 0.90 before and after immersion in 1.0 M H_2SO_4. The Tafel slopes
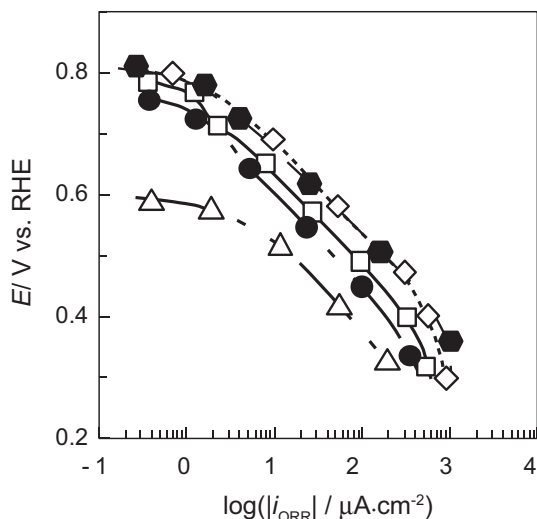
Fig. 1. Concentration of Zr on Zr–CNO before and after immersion as a function of the degree of oxidation in 1.0 M H_2SO_4 (■: Zr on Zr_2CN, □:Zr on Zr–CNO, ▣:Zr on ZrO_2 (commercial)).

Fig. 3. Tafel plots for ORR of Zr−CNO before and after immersion in 1.0 M H$_2$SO$_4$ (- ◇ -: *DOO* of 0.99 after 45-day immersion, —●—: *DOO* of 0.99 after 28-day immersion, —□—: *DOO* of 0.99 before immersion, —●—: *DOO* of 0.45 before immersion, —△ -: *DOO* of 0.25 before immersion).

Fig. 5. Dependence of *i** of Zr−CNO on immersion time in 1.0 M H$_2$SO$_4$ (○: *DOO* of 0.45, □: *DOO* of 0.99, Δ: *DOO* of 0.25).

of the ORR of Ta−CNO before and after the immersion in sulfuric acid in all the |i_{ORR}| regions were almost the same. This was suggested that the reaction mechanism for the ORR on Ta−CNO might not change before and after the immersion in the sulfuric acid.

In order to investigate the specific activities of both Ta−CNO and Zr−CNO before and after the immersion, the electrochemical surface area should be evaluated. However, it is difficult to evaluate the electrochemically active surface area of an oxide and oxide-based compound. Though the electric charge depends on the surface state and structure of the electrode, it could be used as the parameter of the pseudo-surface area as in the case of industrial electrolysis [9,10]. In this study, we also define the pseudo-current density: *i** which is the |i_{ORR}| at 0.65 V divided by the anodic electric charge calculated from the cyclic voltammogram in the potential range from 0.3 to 0.8 V. Fig. 5 shows the dependence of the *i** for the
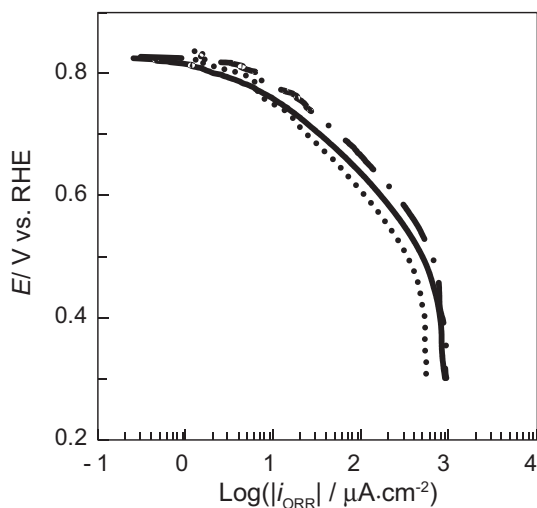
Zr−CNO on the immersion time in sulfuric acid. The *i** on the Zr−CNO with the *DOO* value of 0.45 and 0.99 after a 28-day immersion was almost one-third of that before the immersion. Especially, the *i** on the Zr−CNO with the *DOO* of 0.99 after a 28-day immersion decreased to almost the same value as that on Zr−CNO with the *DOO* of 0.25 after the 28-day immersion. Since the *i** on the Zr−CNO with the *DOO* of 0.25 hardly changed before and after the 28-day immersion, the catalytic activity for the ORR might also be constant. In other words, the catalytic activity for the ORR of Zr−CNO with the *DOO* of 0.99 after the 28-day immersion became smaller than that before the immersion and almost the same as that with the *DOO* of 0.25. As shown in Fig. 3 at the smaller |i_{ORR}| region, the Tafel slopes on Zr−CNO with the *DOO* of 0.99 after the immersion changed to a value that was almost the same as that with the *DOO* of 0.25 before the immersion in the sulfuric acid. These facts agreed with those shown in Fig. 5. Therefore, the catalytic activities for the ORR of Zr−CNO with the *DOO* of 0.45 and 0.99 deteriorated when immersed in the sulfuric acid.

Fig. 6 shows the dependence of the *i** of Ta−CNO with the *DOO* of 0.90 on the immersion time in the sulfuric acid. The *i** of Ta−CNO

Fig. 4. Tafel plots for ORR of Ta−CNO (*DOO* of 0.90) before and after immersion in 1.0 M H$_2$SO$_4$ (— · —: after 30-day immersion, ——: before immersion, ——————: after 45-day immersion).
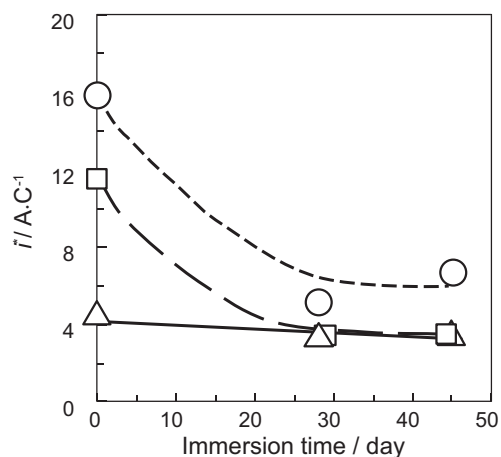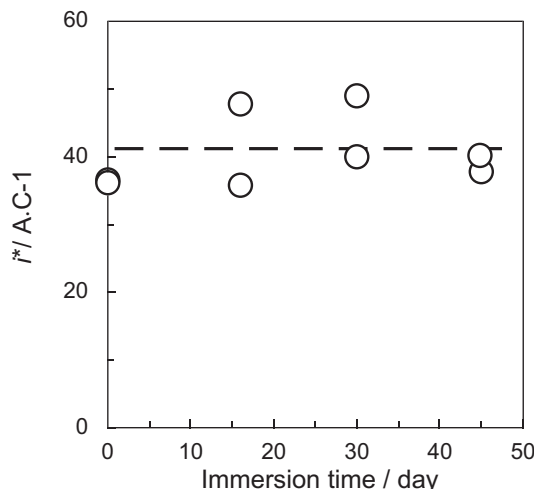

Fig. 6. Dependence of *i** of Ta−CNO (*DOO* of 0.90) on immersion time in 1.0 M H$_2$SO$_4$.

was almost constant vs. the immersion time. These facts agreed with the facts shown in Fig. 3. Because of the high chemical stabilities and constant Tafel slope of the ORR on Ta—CNO, the catalytic activities for the ORR of Ta—CNO remained constant during the immersion for 1050 h in the sulfuric acid.

4. Conclusions

Above all, the dissolution amount of Zr on Zr—CNO was higher than that of Pt on Pt black, and the catalytic activities for the ORR on Zr—CNO with the *DOO* value of 0.45 and 0.99 deteriorated by their immersion in the sulfuric acid. In contrast, the dissolution amounts of Ta on Ta—CNO was almost the same or lower than that of Pt on Pt black, and the catalytic activity for the ORR on Ta—CNO with the *DOO* of 0.90 was maintained up to 1050 h in the sulfuric acid.

Compared with Zr—CNO, Ta—CNO has a good stability and could be used as a new cathode of PEFCs with an increased catalytic activity for the ORR.

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